In-situ non destructive testing of cementitous materials via embedded ultrasonic transducers made up of carbon nanotubes.

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Abstract

In-situ instrumentation enables better prediction of the aging of structures than the commonly used visual inspections and "just-in-time" prevention of accidents linked to failures. To reach its full development, this science is in dire need for cheap wireless micro (or even nano) sensors immersed by the thousands in the concrete of every new structure. Demonstrating than such micro-sensors are actually embeddable into cementitous materials and can provide the user with valuable information on the material under test will be a major breakthrough.

A step toward this long-term goal, we describe in this paper an innovative high frequency capacitive micromachined transducer (cMUT) based on a membrane of aligned carbon nanotubes. To this day, we have realized potentially suitable membranes. They are being characterized. By modeling, we have determined that such device, used in water from about 50 MHz to 5 GHz, could measure pores in the 10 nm to 10µm range.

Résumé

Le suivi in-situ des matériaux est essentiel à la prédiction du vieillissement des constructions et à la prévention en temps réel de leurs défauts. Cette science a besoin de micro (voire nano) capteurs autonomes, économiques, et surtout implantables en grand nombre dans les matériaux cimentaires. La démonstration que de tels capteurs sont effectivement immergeables et qu'ils fournissent des informations exploitables constituera une rupture technologique majeure.

En vue de cet objectif à long terme, cet article décrit un nouveau type de transducteur ultrasonique capacitif micromachiné (cMUT). Il s'agit d'un dispositif hautes-fréquences dont la membrane vibrante est constituée de nanotubes de carbone alignés. A ce jour, nous avons réalisé des membranes potentiellement adaptées à l'application visée. Les caractérisations sont en cours. Par ailleurs, notre modélisation a établi qu'un tel dispositif cMUT, utilisé dans l'eau entre 50 MHz et 5 GHz environ, pourrait mesurer les dimensions de pores dans une gamme comprise entre 10 nm et 10 µm.

Keywords

cMUT, membrane, dielectrophoresis, high-frequency, porosimetry

1 Introduction

Microporosity is a key point to the precise understanding and monitoring of cement-based materials in a durability perspective. In this paper, we first briefly recall the main existing porosity evaluation methods, and then describe an innovative device for in-situ, embedded monitoring of the microporosity. We present several elements of its implementation into cementitous materials.

2 Durability assessment via porosity evaluation

2.1 A performance-based durability approach

Durability aims at preventing any kind of degradations likely to hinder the regular use of infrastructures and buildings. Carbonatation [1], frost, or alkali-reactions [2] are typical examples. They lead to swelling, inducing additional stresses in the structures, and cracks may open. These degradations depend on different internal and environmental factors. Among them, the material porosity has a decisive impact, either directly or indirectly, via ionic and gas transfer within the material [3].

Long-term laboratory tests and field studies have led to the definition of classes of durability for any given reinforced concrete according to a set of indicators correlated to the porosity, such as porous fraction, permeability, and diffusivity. Concurrently, classes of environment have been defined according to external parameters, such as humidity and concentration in chloride ions. Building codes (for instance *NF P 18-305*, *NF EN 206-1 …)* now normatively set the class of concrete to be used depending on the class of environment and the life expectancy of the structure. [4]

2.2 Performances and limits of existing porosity evaluation method

A precise knowledge of porosity is essential for this durability approach to be efficient. Mercury porosimetry is a very widely used method [5]. However, there are known biases [6], such as the mandatory drying of samples before measurement and the use of high Mercury pressures. Interpretation of the measurements is conditioned by rough hypotheses on pore shape and accessibility. Porosimetry by gas adsorption [7], although sensitive to sub-nanometer pore sizes, has similar drawbacks. Small scale imaging methods, like RMN, SEM and TEM, SANS and SAXS [8] have exceptional resolutions, but the samples preparation is very demanding.

The repartition of porous volume ranges mostly from a few micrometers down to a few angstroms, as exhibited by these multi-scale methods. The pores down to about 10 nm size, i.e. the capillary pores, are of various shapes. They are post-hydration residues of the space between anhydrous grains. Their impact on durability analysis is most significant [7].

However, methods for in-situ, non destructive testing of capillary porosity are not widely developed. Next section describes an innovating concept of embedded instrumentation adapted to the in-situ study of capillary pores.

3 A new ultrasonic, micro-scale investigation method of the porosity

3.1 Instrumentation strategy: Gigahertz ultrasonic embedded monitoring

Cementitous materials are highly heterogeneous. Multiple sensors are needed for their comprehensive survey. For each of them, we maximize the individual probed volume and use a wave propagation strategy, thus reducing the number of needed devices and limiting the perturbations induced by their embedding.

Both electromagnetic and acoustic waves could be used. The actual wavelength has to be on the micrometer scale to be compatible with the targeted microporosity features. So, suitable electromagnetic waves would be in the Terahertz range, while acoustic waves may be at frequencies lower than a few Gigahertz, especially as we only consider waves that propagate within the air or water filled micro-pores. Such frequencies are of common use in microelectronics.

High-frequency (up to 200 MHz) ultrasonic transducers have been developed by other labs [9]. However, producing such devices at the micrometer scale and in the Megahertz range is still challenging [10]. By using nanotechnologies, we will be able to simultaneously downsize the devices and increase their resonance frequency.

3.2 A Carbon Nanotubes based device

High frequency resonators (1.33 GHz in vacuum) have been realized by Zettl's group [11] from individual carbon nanotubes suspended over 100 nm to 1 micrometer wide trenches. The nanotubes are actuated through a back-gate electrode. The advantage of carbon nanotubes for this application lays in their extremely high Young's modulus (1 THz theoretical, 500 MHz measured).

We will adapt these devices to enable proper actuation of fluid media. We propose a novel, high-frequency, capacitive, micro-machined, ultrasonic transducer based on a membrane of densely aligned carbon nanotubes, as shown in figure 1 (patent pending [12]). The typical dimension of the cMUT membrane ranges from 300 nm up to 2 microns. It is only a few nanotubes thick, roughly 1 to 15 nm. Preliminary modeling (to be published) based on the one-dimensional non-linear modeling of carbon nanotubes indicates that such a device could work at frequencies higher than 1 GHz (up to about 5 GHz) in vacuum.

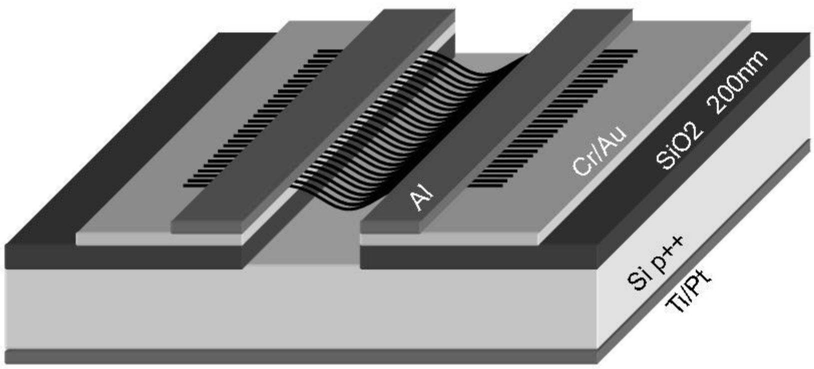

Figure 1: *Schematic technological design of a carbon nanotubes based cMUT device.*

3.3 Fluid-structure interaction

Experimental results on individual suspended nanotubes demonstrate that, compared to vacuum, working in air at atmospheric pressure has a limited impact on the resonance frequencies (around 1% frequency shift) [13]. However, in water, the resonance frequency decreases considerably [10]. To define the actual range of the magnitude of the resonance frequency in water, we are developing a specific, two-dimensional numerical model (to be also published).

We consider a 1 µm-long embedded beam representing the membrane section. The Young's modulus E is 1 TPa and the thickness h is 1 nm. It is submitted to a sinusoidal stress F.cos(ωt) ($F \approx 1$ mN/m²) and it follows the Euler Bernoulli equation. It actuates water in a closed cavity that stands for a pore section (figure 2a). We assume that the water is at atmospheric pressure and room temperature. These hypotheses may need to be refined in further work to take into account potentially strong gradients within the material. The water obeys the linearized Navier Stokes equations. Water velocity distribution is computed via a finite element method, and the displacement of the beam via modified Fourier series. Work is still in progress on this model.

For a thin beam (h<5 nm), vibrations do not depend on the beam characteristics. When sweeping frequencies, one observes only the cavity eigenmodes. For thicker beams, beam eigenmodes appear because the mass ratio between beam and load increases.

The vibration amplitudes depend strongly on cavity depths (figure 2b). However, any given amplitude can correspond to a set of different cavity sizes, so measurements at two different frequencies will be needed to univocally determine the cavity depth.

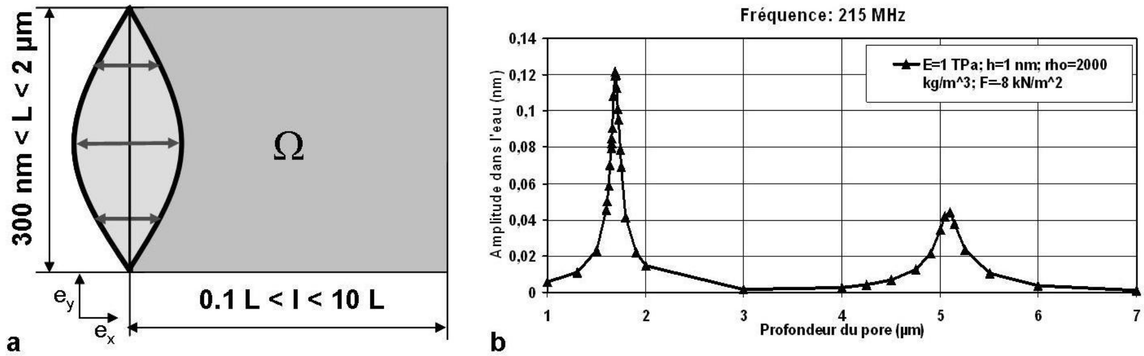

Figure 2: *a) Model 2D geometry b) Résonances depending on cavity length*

4 Implementation of the device

4.1 Read-out of the device

The readout of our nanotube-based cMUT device is the total variable capacity between membrane and electrode. This capacity has a constant part of about 50 aF (5.10^{-17}) for a 1µm² membrane at distance of 200 nm from the counter-electrode. For average displacements of 1 nm, the variable part accounts to about 0.5 % of the constant capacity.

The measurement of this small variable capacity requires careful minimization of noise and amplification stages. Several teams are currently developing a generic methodology to address this metrological concern as in [13], and it will eventually address frequencies above 1 GHz. We will then be able to derive the average displacements of the device membrane from the capacity measurement, and deduce pore sizes.

4.2 Experimental achievements

At this time, we have defined a process, based on the dielectrophoresis of carbon nanotubes in solution, to align nanotubes in a thin membrane. We have realized potentially suitable membranes that are being characterized (figure 3). To actuate water or air as required by the application, they may need an additional deposition of few-layers graphene [14] making them water- and airtight.

Next technological steps involve integration of the membranes into a device with built-in electronics.

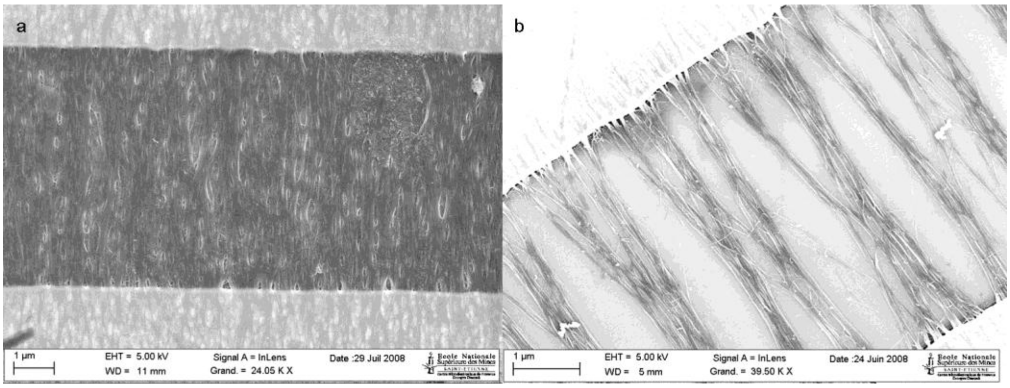

Figure 3: *Aligned carbon nanotubes membranes a) high density b) low density.*

4.3 Implementation into cementitous materials (Patent pending [15])

For embedded instrumentation of a cementitous material, the sensing device needs associated antenna, computation unit and power supply. On the long term, the targeted device is a micrometer-sized, autonomous and wireless device randomly positioned within the studied material for in-situ non destructive testing. In early feasibility demonstrators, only the sensor itself will be downsized. Peripheral functionalities will first be provided by macroscopic features.

The demonstrator will thus be a macroscopic sensing module, so its volume will let us provide not only for one, but for a network of identical micrometer-size cMUT sensors, each of them monitoring a small part of the surrounding microporosity.

To limit mechanical or chemical perturbations of the material, this module should be designed with dimensions smaller than the inter-aggregates average distance and smaller than the aggregates average size, and equipped with a shell chemically compatible with the aggregates. The implementation of an appropriate density of these modules will provide with localized, embedded and in-situ data on the material microporosity.

5 Conclusions

We have described an innovative high-frequency cMUT device based on a membrane of aligned carbon nanotubes. It is specifically designed to address the in-situ embedded monitoring of the microporosity of cementitous materials. As a first step toward a demonstrator, we have realized carbon nanotubes membranes. By modeling, we have determined that, working between about 50 MHz and 5 GHz in water, the device could be used for a 10 nm to 10 µm porosimetry of cementitous materials.

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